



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> ELECTROLUMINESCENT MATERIAL		
<b>(57) Abstract</b> <p>Electroluminescent devices with a high photoluminescent efficiency comprise a transparent conductive substrate on which is formed a layer of an electroluminescent material in which the electroluminescent material is a rare earth metal, actinide or transition metal organic complex which has a photoluminescent efficiency (PL) of greater than 25 %.</p>		

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### Electroluminescent Material

The present invention relates to electroluminescent materials and to devices incorporating them.

Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used, however these suffer from the disadvantages of high energy consumption, high cost of manufacture, low quantum efficiency and the inability to make flat panel displays.

Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

In an article in Chemistry letters pp 657-660, 1990 Kido et al disclosed that a terbium III acetyl acetonate complex was green electroluminescent and in an article in Applied Physics letters 65 (17) 24 October 1994 Kido et al disclosed that a europium III triphenylene diamine complexes was red electroluminescent but these were unstable in atmospheric conditions and difficult to produce as films.

The complexes disclosed in these articles had a low photoluminescent efficiency and were only able to produce green or red light and other colours could not be produced.

We have now discovered electroluminescent materials which have a higher photoluminescent efficiency and which can produce a range of colours, which has hitherto been difficult to produce.

The higher photoluminescent efficiency enables these materials to be used in a range of applications.

According to the invention there is provided an electroluminescent device comprising a transparent substrate on which is formed a layer of an electroluminescent material in which the electroluminescent material is a rare earth metal, actinide or transition metal organic complex which has a photoluminescent efficiency (PL) of greater than 25%.

The photoluminescent efficiency is a measure of the efficiency of conversion of absorbed light to emitted light and can be measured as described in the Article in Chemical Physics Letters 241 (1995)89-96 by N.C. Greenham et al.

Another measure which has been used for measuring efficiencies is based on the consumption of electricity by the material (the electroluminescent efficiency).

The metal complexes of the present invention have the formula  $X(Y_1)(Y_2)(Y_3)$  where X is a rare earth, transition metal, lanthanide or an actinide in the III state and  $Y_1$ ,  $Y_2$ ,  $Y_3$  are the same or different organic complexes. When the metal is in the II state e.g. Eu II, there will be two Y groups and when the metal is the IV state there will be four Y groups.

Rare earth chelates are known which fluoresce in ultra violet radiation and A. P. Sinha (Spectroscopy of Inorganic Chemistry Vol. 2 Academic Press 1971) describes several classes of rare earth chelates with various monodentate and bidentate ligands.

Group III A metals and lanthanides and actinides with aromatic complexing agents have been described by G. Kallistratos (Chimica Chronika, New Series, 11, 249-266 (1982)). This reference specifically discloses the Eu(III), Tb(III) and U(III) complexes of diphenyl-phosponamidotriphenyl-phosphoran.

EP 0744451A1 also discloses fluorescent chelates of transition or lanthanide or actinide metals.

The known chelates which can be used are those disclosed in the above references including those based on diketone and triketone moities.

In order to produce a material with a high PL and which electroluminesces at the desired colour, the nature of the ligand and the metal are specifically chosen.

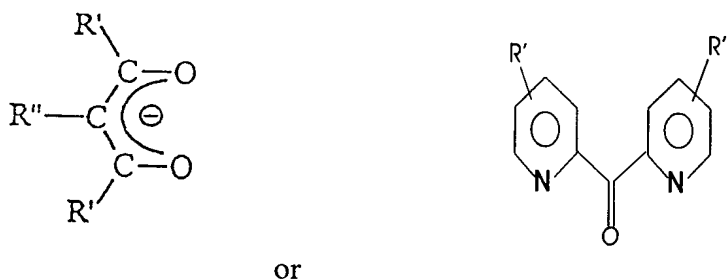
Preferably a metal ion having an emission frequency and a resonant frequency with efficient transition between these frequencies are chosen and the ligand has a triplet energy level slightly above the resonant level of the metal ion.

Preferably the triplet state of the ligand or chelate is no greater than 0.7 eV the resonant frequency of the metal ion and more preferably no greater than 0.4eV above the resonant frequency of the metal ion. Suitable ranges are from 0.1 to 0.7eV.

This is diagrammatically illustrated in fig.1 of the accompanying drawings

Any metal ion having an unfilled inner shell can be used as the metal and the preferred metals are Sm(III), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Eu(II), Gd(III) U(III), UO<sub>2</sub>(VI), Th(III)

Preferred chelating groups have the formula



where R' maybe the same or different at different parts of the molecule and each of R'' and R' is an aromatic or heterocyclic ring structure which may be substituted or a hydrocarbyl of a fluorocarbon or R'' is a halogen such as fluorine or hydrogen. R'' can also be copolymerisable with a monomer e.g. styrene R' can be t-butyl and R'' hydrogen.

Examples of metal chelates are (a) terbium (III) dipivaloyl methide)<sub>3</sub>, known as terbium tris(2,2,6,6-tetramethyl 3,5 heptanedionate) chelate, (b) di- and tri-pyrazolyl borate and the di- and tri-pyrazolyl-N-oxide borate adducts of (a), (c) europium (III) (2-naphthyl trifluoro acetyl acetonate) or (d) uranyl (2-naphthyl trifluoro acetyl acetonate) or the dipyriddy and dipyriddy N-oxide adducts of (c) and (d).

EP 0744451A1 discloses fluorescent compounds which are complexes of transition, metal, lanthanide and actinide chelates and methods for making these, it has been found that these complexes are electroluminescent and by the selection of the metal ion and complex as referred to above a high efficiency electroluminescent material of a specific colour can be prepared.

The devices of the invention comprise a transparent substrate which is a conductive glass or plastic material which acts as the cathode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate. The electroluminescent material can be deposited on the substrate directly by evaporation from a solution of the material in an organic solvent. The solvent which is used will depend on the material but chlorinated hydrocarbons such as dichloromethane are suitable in many cases.

Alternatively the material can be deposited by spin coating or by vacuum deposition from the solid state e.g. by sputtering or any other conventional method can be used.

In one embodiment of the invention there is a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

Hole transporting layers are used in polymer electroluminescent devices and any of the known hole transporting materials in film form can be used.

The hole transporting layer can be made of a film of an aromatic amine complex such as poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), polyaniline etc.

The hole transporting material can optionally be mixed with the electroluminescent material in a ratio of 5 - 95% of the electroluminescent material to 95 to 5% of the hole transporting compound.

In another embodiment of the invention there is a layer of an electron injecting material between the cathode and the electroluminescent material layer, this electron injecting material is preferably a metal complex such as a metal quinolate e.g. an aluminium quinolate which will transport electrons when an electric current is passed through it. Alternatively the electron injecting material can be mixed with the electroluminescent material and co-deposited with it.

In a preferred structure there is a substrate formed of a transparent conductive material which is the anode on which is successively deposited a hole transportation layer, the electroluminescent layer and an electron injection layer which is connected to the anode. The anode can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc., aluminium is a preferred metal.

It is a feature of the invention that by forming a layer on the substrate which is a mixture of electroluminescent materials which emit different colour light the emitted light will have a colour which is an additive colour of the individual colours.

Another feature of the invention is that by having a plurality of layers emitting different colour light sequentially deposited on the substrate a light which is an additive combination of the individual colours is emitted, thus by having layers which emit green, red and blue light, white light will be emitted.

In this structure the thickness of the layers are chosen so that recombination of electrons and holes on passage of an electric current takes place in the electroluminescent layer.

In general the thickness of the layers is from 20nm to 200nm.

It is possible to co-deposit mixtures of the electroluminescent metal complexes from solution so that the colour of the emitted light can be modified, in this way the desired colours can be selected.

The electroluminescent devices of the present invention give light with a narrow wave band with a very bright emission and it is possible to emit light in a range of colours.

Schematic diagrams of devices according to the invention are illustrated in figs. 13a, 13b, 13c and 13d. In these drawings (1) is the emissive layer, (2) is ITO, (3) is an electron transporting layer and (4) is a hole transporting layer.

The invention is described in the following Examples

#### 1. Device Fabrication

An ITO coated glass piece ( $1 \times 1\text{cm}^2$  cut from large sheets purchased from Balzers, Switzerland) had a portion etched out with concentrated hydrochloric acid to remove the ITO and was cleaned and placed on a spin coater (CPS 10 BM, Semitec, Germany) and spun at 2000 rpm for 30 seconds, during which time the solution of the electroluminescent compound was dropped onto it dropwise by a pipette.

Alternatively the electroluminescent compound was vacuum evaporated onto the ITO coated glass piece by placing the substrate in a vacuum coater and evaporating the electroluminescent compound at  $10^{-5}$  to  $10^{-6}$  torr onto the substrate.

The organic coating on the portion which had been etched with the concentrated hydrochloric acid was wiped with a cotton bud.

The coated electrodes were stored in a vacuum desiccator over calcium sulphate until they were loaded into a vacuum coater (Edwards,  $10^{-6}$  torr) and aluminium top contacts made. The active area of the LED's was  $0.08\text{ cm}^2$  -  $0.1\text{ cm}^2$  the devices were then kept in a vacuum desiccator until the electroluminescence studies were performed.



The ITO electrode was always connected to the positive terminal.

The current vs. voltage studies were carried out on a computer controlled Keithly 2400 source meter.

Electroluminescence spectra were recorded by means of a computer controlled charge coupled device on Insta Spec photodiode array system model 77112 (Oriel Co., Surrey, England)

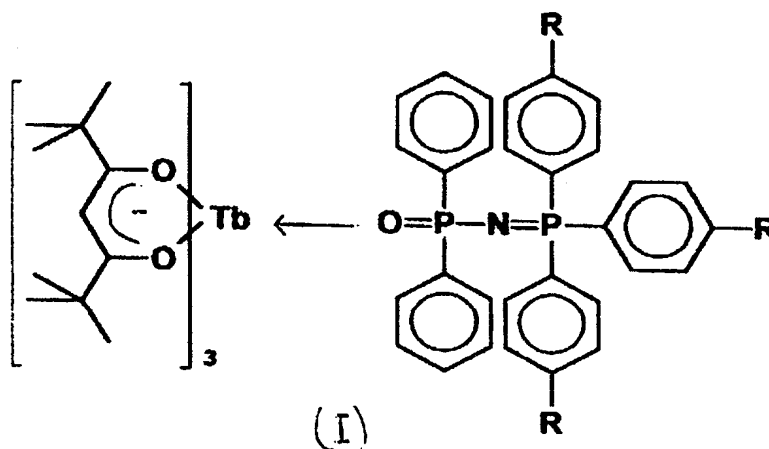
## 2. Photoluminescence Measurements

Photoluminescence was excited using 325nm line of Liconix 4207 NB, He/Cd laser. The laser power incident at the sample ( $0.3\text{mWcm}^{-2}$ ) was measured by a Liconix 55PM laser power meter. The radiance calibration was carried out using Bentham radiance standard (Bentham SRS8, Lamp current 4,000A, calibrated by National Physical laboratories, England. The PL studies were carried out on samples or films.

Examples 2 to 12 are examples of the synthesis of electroluminescent compounds of the invention and Example 1 is an example of the known complex

### Example 1

Tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III)  $[\text{Tb}(\text{TMHD})_3]$  di phenyl phosponimide tris-phenyl phosphorane - in (I) R is H.



[Tb(TMHD)<sub>3</sub>] (1mM) was mixed with 1mM of diphenylphosphinic-azide in 5 ml trimethyl pentane and the mixture heated to reflux until a clear solution was obtained (about 1 hour). The solution was allowed to clear yielding tris (2,2,6,6-tetramethyl-3,5- heptanedionato) Terbium (III) di phenyl phosponimide tris-phenyl phosphorane as a crystalline solid m.p. 246-248°C in nearly quantitative yield.

#### Example 2

Tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) phosponimide tris-(tolylphenyl) phosphorane - in (I) R is CH<sub>3</sub>

Tris-(2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) (0.2g, 0.28mmol) and diphenyl phosponimide tris -(tolylphenyl) phosphorane ( 0.145g, 0.28 mmol) was heated at reflux in 2,2,4-trimethyl pentane until all solid went into solution (ca 3 hours) Then the solution was allowed to cool to room temperature The resultant precipitate was filtered off and dried in vacuo at 50°C to yield a white solid (0.211g) which was tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) phosponimide tris-(tolylphenyl) phosphorane m.p. 94-98°C.

#### Example 3

Tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) diphenyl phosponimide tris-(methoxyphenyl) phosphorane - in (I) R is OCH<sub>3</sub>

Tris- (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) (0.2g, 0.28mmol) and diphenyl phosponimide tris -(methoxyphenyl)- phosphorane (0.159g, 0.28mmol) was heated at reflux in 2,2,4-trimethyl pentane until all solid went into solution (ca 3 hours) Then the solution was allowed to cool to room temperature. The resultant precipitate was filtered off and dried in vacuo at 50°C to yield a white solid (0.211g) which was tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) diphenyl phosponimide tris-(methoxyphenyl) phosphorane.

#### Example 4

Tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) diphenyl phosponimide tris-(fluorophenyl) phosphorane - in (I) R is F.

Tris- (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) (0.2g, 0.28mmol) and diphenyl phosponimide tris -(fluorophenyl) phosphorane ( 0.157g, 0.28mmol) was heated at reflux in 2,2,4-trimethyl pentane until all solid went into solution (ca 3 hours) Then the solution was allowed to cool to room temperature. The resultant precipitate was filtered off and dried in vacuo at 50°C to yield a white solid (0.226g) which was tris (2,2,6,6- tetramethyl-3,5- heptanedionato) Terbium (III) diphenyl phosponimide tris-(fluorophenyl) phosphorane m.p. 104-108°C.

#### Example 5

Tris (2,2,6,6'-tetramethyl-3,5-heptanedionato) terbium(III) mono-di-(2-pyridyl) ketone.

Tris (2,2,6,6'-tetramethyl-3,5-heptanedionato) terbium(III) (0.71g 1mmol) was dissolved in ethanol (100ml) at 40 °C whilst stirring. Di-(2-pyridyl) ketone (0.18g, 1mmol) was added. The mixture was stirred for 1 hour and the clear yellow solution dried in vacuo to give a pale yellow product (0.84g) which was Tris (2,2,6,6'-tetramethyl-3,5-heptanedionato) terbium(III) mono-di-(2-pyridyl) ketone (Yield 84%).

#### Example 6

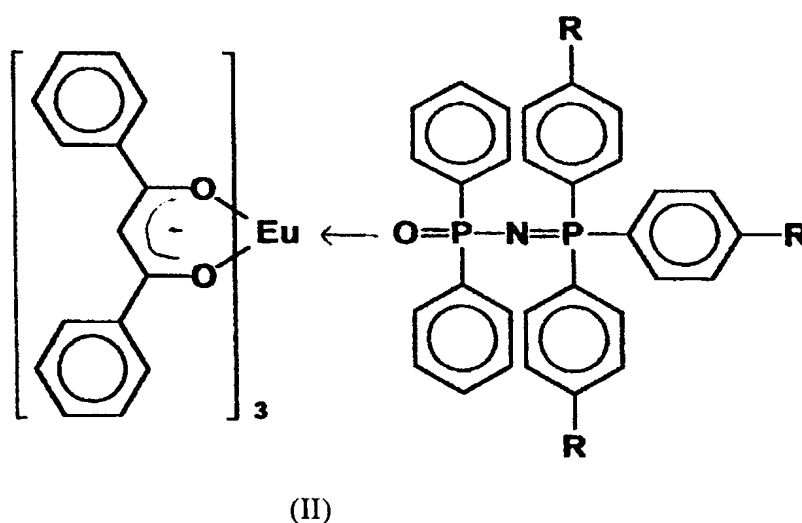
Europium (III) dibenzoyl methane (DBM) diphenyl phosphonimide triphenyl phosphorane

Europium (III) (DBM) (0.5g, 60.2 mmol) and diphenyl phosphonimide triphenyl phosphorane (OPNP) (0.574g, 1.294 mmol) were melted together at 200°C in an oven and held at that temperature for 1 hour. The resultant mixture was dissolved in hot toluene (10ml) and added dropwise to cold (ice/water) trimethylpentane (150ml) to precipitate the complex. The precipitate was filtered off and dried in vacuo at 50°C to

yield a yellow solid (0.72g) which was Europium (III) dibenzoyl methane diphenyl phosphonimide triphenyl phosphorane m.p. 272-276°C.

### Example 7

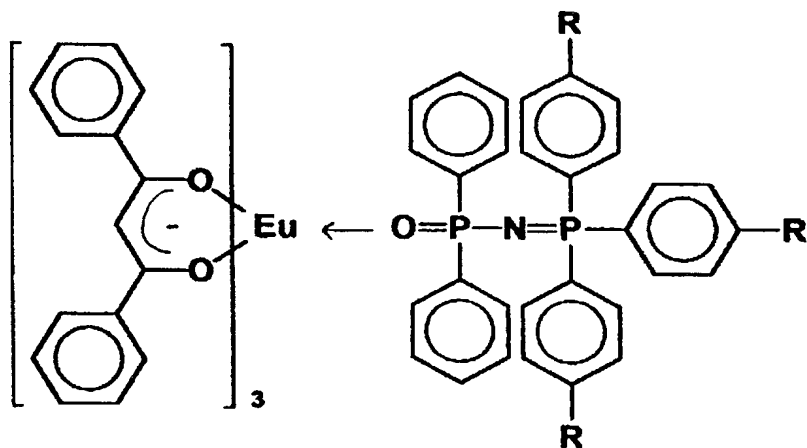
Europium (III) dibenzoyl methane (DBM) diphenyl phosphonimide tris(methoxyphenyl) phosphorane - in (II) R is OCH<sub>3</sub>



Europium (III) (DBM) (0.5g, 0.602 mmol) and diphenyl phosphonimide trismethoxy phosphorane (OPNPCH<sub>3</sub>) (0.683g, 1.20 mmol) were melted together at 200°C in an oven and held at that temperature for 1 hour. The resultant mixture was dissolved in hot toluene (10ml) and added dropwise to cold (ice/water) trimethylpentane (150ml) to precipitate the complex. The precipitate was filtered off and air dried to yield a yellow solid (0.503g) which was Europium (III) dibenzoyl methane diphenyl phosphonimide trismethoxy phosphorane m.p. 150-154°C

Example 8

Europium (III) dibenzoyl methane (DBM) diphenyl phosphonimide tris(fluorophenyl) phosphorane - in (II) R is F.

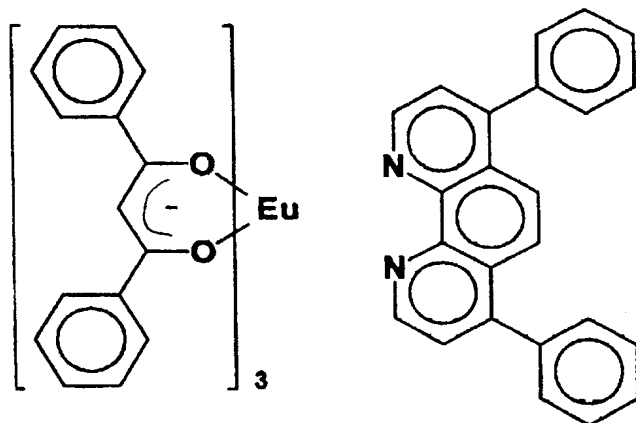


(II)

Europium (III) (DBM) (0.285g, 0.343 mmol) and diphenyl diphenyl phosphonimide trisfluoro phosphorane (OPNPF) (0.385g, 0.686 mmol) were melted together at 200°C in an oven and held at that temperature for 1 hour. The resultant mixture was dissolved in hot toluene (10ml) and added dropwise to cold (ice/water) trimethylpentane (150ml) to precipitate the complex. The precipitate was filtered off and air dried to yield a yellow solid (0.562g) which was Europium (III) dibenzoyl methane diphenyl phosphonimide trisfluoro phosphorane m.p. 218-222°C

Example 9

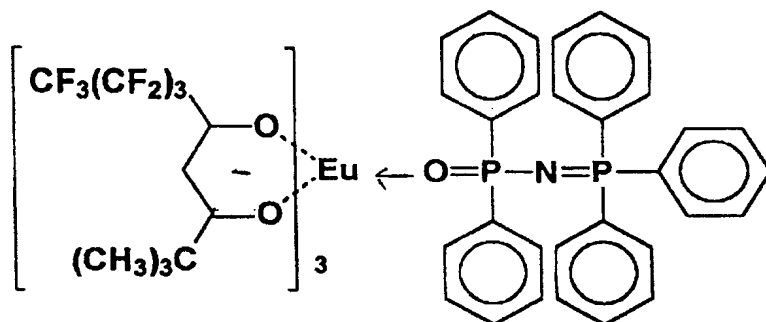
Europium (III) dibenzoyl methane (DBM) 4,7-diphenyl-1, 10-phenanthroline



Europium (III) dibenzoyl methane (DBM) (0.5g, 0.6mmol) was heated at reflux with 4,7-di[phenyl-1, 10 phenanthroline (0.2g 0.6mmol) in chloroform (5ml) overnight. The solvent was removed in vacuo to yield an orange solid (0.66g) which was europium (III) dibenzoyl methane (DBM) 4,7-diphenyl-1, 10-phenanthroline m.p. >250°C

Example 10

Europium (FOD) OPNP



Europium FOD (0.5g, 0.482 mmol) and OPNP (0.230g, 0.484 mmol) was dissolved in chloroform (15ml) and the resulting solution heated at reflux overnight. The solvent was removed in vacuo to yield a yellow solid which was europium (FOD) OPNP m.p. 212-214°C

#### Example 11

Tris (2,2,6,6- tetramethyl-3,5- heptanedionato) dysprosium (III) diphenyl phosponimido triphenylphosphorane.

Tris (2,2,6,6- tetramethyl-3,5- heptanedionato) dysprosium (III) (6.1g, 19.5 mmole) and diphenyl phosponimido triphenylphosphorane. (4.6g, 9.5 mmole) were refluxed in trimethylpentane (60ml) for 30 minutes . The reaction mixture was the allowed to cool to room temperature. A white crystalline material formed on standing. This was recrystallised from diethyl ether to give tris (2,2,6,6- tetramethyl-3,5- heptanedionato) dysprosium (III) diphenyl phosponimido triphenylphosphorane yield : 8 gm., pt.154°C)

#### Example 12

Bis (imidotetraphenyldiphosphinic acid) Uranium dioxide.

Imidotetraphenyldiphosphinic acid (4.3g, 10.3mmole) and sodium hydroxide (0.412g, 10.3 mmole)were heated to 60°C in 90% aqueous ethanol (100ml). Uranyl acetate was then added quickly and the reaction mixture heated to reflux for 20 minutes. the reaction mixture was cooled to room temperature, filtered, washed with ethanol (300ml) and dried under vacuum to give a yellow solid which was bis (imidotetraphenyldiphosphinic acid) Uranium dioxide ( yield 4.4g).

The products of Examples 1 to 11 were formed into devices and their Photoluminescent Efficiency was measured according to the method described in the Article in Chemical Physics Letters 241 (1995)89-96 by N.C. Greenham et al and the results are shown in Table 1.

Table 1

Example	Photoluminescent Efficiency
1	85%
2	90%
3	90%
4	95%
5	40%
6	90%
7	30%
8	55%
9	64%
10	43%
11	77%
12	87%

Tb(TMHD)<sub>3</sub> had a photoluminescent efficiency of 25%, terbium (III) acetyl acetonate complex had a photoluminescent efficiency of 20% and europium (III) phenanthranene complex had a photoluminescent efficiency of 19%.

The spectra are shown in figs. 1 to 11 which show the colours and narrow frequency band of the compounds.

In Tb(TMHD)<sub>3</sub>, terbium (III) acetyl acetonate complex and europium (III) phenanthranene complex the difference between the triplet state of the ligand and the excited states of the metal ion was in order of > 0.6 eV in the compounds of the invention the difference was of the order of < or = to 0.4eV in the case of the terbium complexes and < or = 0.3 eV in the case of the Europium complexes.

As can be seen photoluminescent materials with high photoluminescent efficiencies can be made.

#### Example 13

Composite devices were made according to fig 13 and their properties measured. The results are given in table 2.



Table 2

System	Applied Voltage/V Volts	Current/A Amps	Brightness cdm <sup>2</sup>	Luminous Efficiency lmw <sup>-1</sup>	CIE Colour	
					x	y
1	15	$11 \times 10^{-3}$	540	$1.6 \times 10^{-2}$	0.31	0.59
2	20	$1.5 \times 10^{-5}$	3600	60	0.31	0.59
3	18	$4 \times 10^{-6}$	1935	137	0.31	0.59
4	27	$9.7 \times 10^{-3}$	1200	2.3	0.31	0.59
5	20	$4 \times 10^{-4}$	441	0.3	0.64	0.35
6	20	$1.0 \times 10^{-3}$	9000	0.4	0.65	0.33
7	25	$1.5 \times 10^{-2}$	50	$6.8 \times 10^{-4}$	0.65	0.33
8	26	$1.4 \times 10^{-2}$	100	$1.4 \times 10^{-3}$	0.47	0.49

In Table 2

The Systems comprised the layers:-

1. ITO| Tb(TMHD)<sub>3</sub>OPNP| Al
2. ITO|TPD| Tb(TMHD)<sub>3</sub>OPNP| Al
3. ITO|TPD| Tb(TMHD)<sub>3</sub>OPNP|AlQ| Al
4. ITO|PANI|Tb(TMHD)<sub>3</sub>OPNP|Al
5. ITO|TPD| Eu(DBM)<sub>3</sub>OPNP| Al
6. ITO|TPD| Eu(DBM)<sub>3</sub>OPNP|AlQ| Al
7. ITO|PANI| Eu(DBM)<sub>3</sub>OPNP| Al
8. ITO|PANI| Dy(DBM)<sub>3</sub>OPNP| Al

Where ITO is indium tin coated glass, PANI is polyaniline ALQ is aluminium trisquinolate and TPD, (TMHD)<sub>3</sub>, OPNP, (DBM)<sub>3</sub> are as in the examples.

## Claims

1. An electroluminescent device comprising a transparent substrate on which is formed a layer of an electroluminescent material in which the electroluminescent material is a rare earth metal, actinide or transition metal organic complex which has a photoluminescent efficiency (PL) of greater than 25%.
2. An electroluminescent device comprising a transparent substrate on which is formed a layer of an electroluminescent material in which the electroluminescent material is a rare earth metal, actinide or transition metal organic complex which has a photoluminescent efficiency (PL) of greater than 40%.
3. An electroluminescent device as claimed in claim 1 or 2 in which the electroluminescent material is a metal complexes of the formula  $X(Y_1)(Y_2)(Y_3)$  where X is a rare earth, transition metal, lanthanide or an actinide in the III state and  $Y_1, Y_2, Y_3$  are the same or different organic ligands.
4. An electroluminescent device as claimed in claim 3 in which the electroluminescent material is a metal complexes of the formula  $X(Y_1)(Y_2)$  where X is a rare earth, transition metal, lanthanide or an actinide in the II state and  $Y_1, Y_2, Y_3$  are the same or different organic ligands.
5. An electroluminescent device as claimed in claim 3 in which the electroluminescent material is a metal complexes of the formula  $X(Y_1)(Y_2)(Y_3)(Y_4)$  where X is a rare earth, transition metal, lanthanide or an actinide in the III state and  $Y_1, Y_2, Y_3, Y_4$  are the same or different organic ligands.
6. An electroluminescent device as claimed in any one of claims 1 to 5 in which the metal is selected from Sm(III), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Eu(II), Gd(III) U(III),  $UO_2(VI)$  and Th(III).
7. An electroluminescent device as claimed in any one of claims 1 to 6 in which the triplet state of the ligand is no greater than 0.6eV above the resonant frequency of the metal ion.

8. An electroluminescent device as claimed in any one of claims 1 to 6 in which the triplet state of the ligand is no greater than 0.4eV above the resonant frequency of the metal ion.

9. An electroluminescent device as claimed in any one of claims 1 to 8 in which the ligand has the formula



or

where R' is the same or different at different parts of the molecule and each R'' and R' is substituted or unsubstituted an aromatic heterocyclic ring structure or a hydrocarbyl or a fluorocarbon or R'' is fluorine or hydrogen or R'' is copolymerised with a monomer e.g. or R' is t-butyl and R'' hydrogen.

10. An electroluminescent device as claimed in any one of claims 1 to 9 in which the electroluminescent material is (a) terbium (III) dipivaloyl methide)<sub>3</sub>, (b) di- and tri-pyrazolyl borate and the di- and tri-pyrazolyl-N-oxide borate adducts of (a) (c) europium (III) (2-naphthyl trifluoro acetyl acetate) or (d) uranyl (2-naphthyl trifluoro acetyl acetate) or the dipyridyl and dipyridyl N-oxide adducts of (c) and (d).

11. An electroluminescent device as claimed in any one of claims 1 to 10 in which there is a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer.

12. An electroluminescent device as claimed in any one of claims 1 to 11 in which there is a hole transporting material mixed with the electroluminescent material in a ratio of 5 to 95% of the electroluminescent material to 95 to 5% of the hole transporting compound.

13. An electroluminescent device as claimed in claim 11 or 12 in which the hole transporting layer is an aromatic amine complex.

14. An electroluminescent device as claimed in claim 13 in which the hole transporting layer is poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD) or polyaniline.

15. An electroluminescent device as claimed in any one of claims 1 to 14 in which there is a metal anode in contact with the electroluminescent material.

16. An electroluminescent device as claimed in any one of claims 1 to 15 in which there is a layer of an electron injecting material between the cathode and the electroluminescent material layer

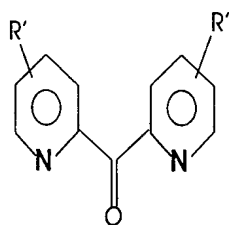
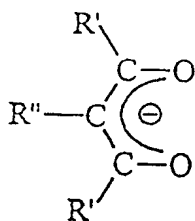
17. An electroluminescent device as claimed in any one of claims 1 to 16 in which an electron injecting material is mixed with the electroluminescent material and co-deposited with it.

18. An electroluminescent device as claimed in claim 16 or 17 in which the electron injecting material is a metal complex or oxadiazole or an oxadiazole derivative.

19. An electroluminescent device as claimed in claim 18 in which the electron injecting material is an aluminium quinolate or 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4 oxadiazole.

20. An electroluminescent device as claimed in any one of the preceding claims in which transparent substrate which is a conductive glass or plastic material which acts as the cathode.

21. An electroluminescent device as claimed in claim 20 in which the substrate is indium tin oxide coated glass.
22. An electroluminescent device as claimed in any one of the preceding claims in which the anode is a metal
23. An electroluminescent device as claimed in claim 22 in which the anode is a aluminium, magnesium, lithium, calcium or a magnesium silver alloy.
24. An electroluminescent device as claimed in any one of the preceding claims in which there are a plurality of layers of electroluminescent material.
25. An electroluminescent device as claimed in any one of the preceding claims in which the layer of electroluminescent material is formed of two or more different electroluminescent compounds.
26. An electroluminescent metal complex of the formula  $X(Y_1)(Y_2)(Y_3)$  where X is a rare earth, transition metal, lanthanide or an actinide in the III state and  $Y_1, Y_2, Y_3$  are the same or different organic ligands at least one of which is



or

and where  $R'$  is the same or different at different parts of the molecule and each  $R''$  and  $R'$  is substituted or unsubstituted an aromatic heterocyclic ring structure or a hydrocarbyl or a fluorocarbon or  $R''$  is fluorine or hydrogen or  $R''$  is copolymerised with a monomer e.g. or  $R'$  is t-butyl and  $R''$  hydrogen and where X is a rare earth, transition metal, lanthanide or an actinide.

27. An electroluminescent metal complex as claimed in claim 26 of the formula  $X(Y_1)(Y_2)$  where X is a rare earth, transition metal, lanthanide or an actinide in the II state.

28. An electroluminescent metal complex as claimed in claim 26 of the formula  $X(Y_1)(Y_2)(Y_3)(Y_4)$  where X is a rare earth, transition metal, lanthanide or an actinide in the IIII state.

29. A complex as claimed in any one of claims 26 to 28 in which the metal is selected from Sm(III), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Eu(II), Gd(III) U(III),  $UO_2$ (VI) and Th(III).

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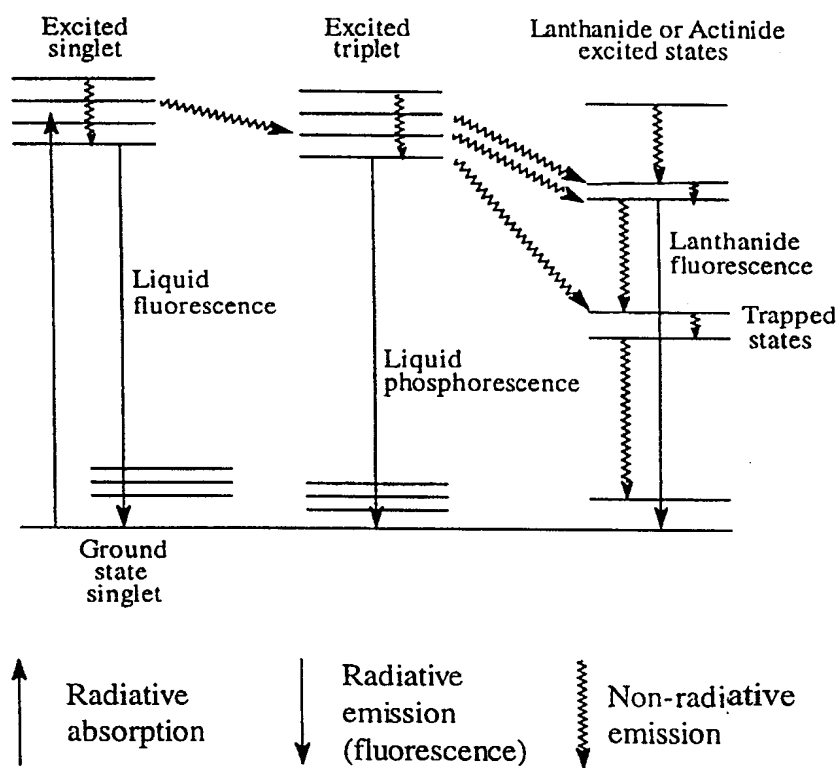
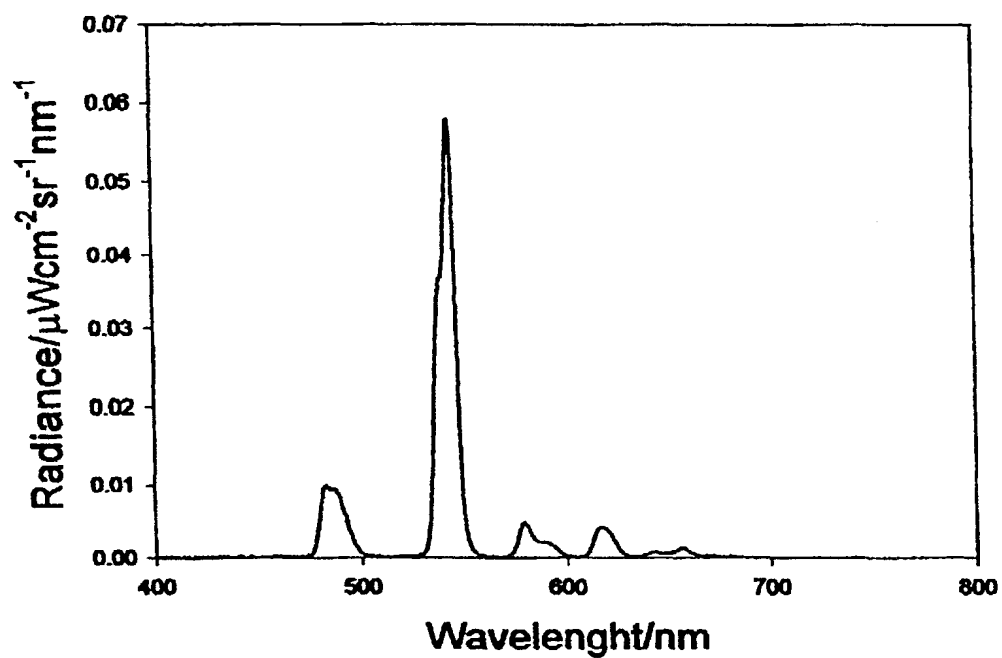
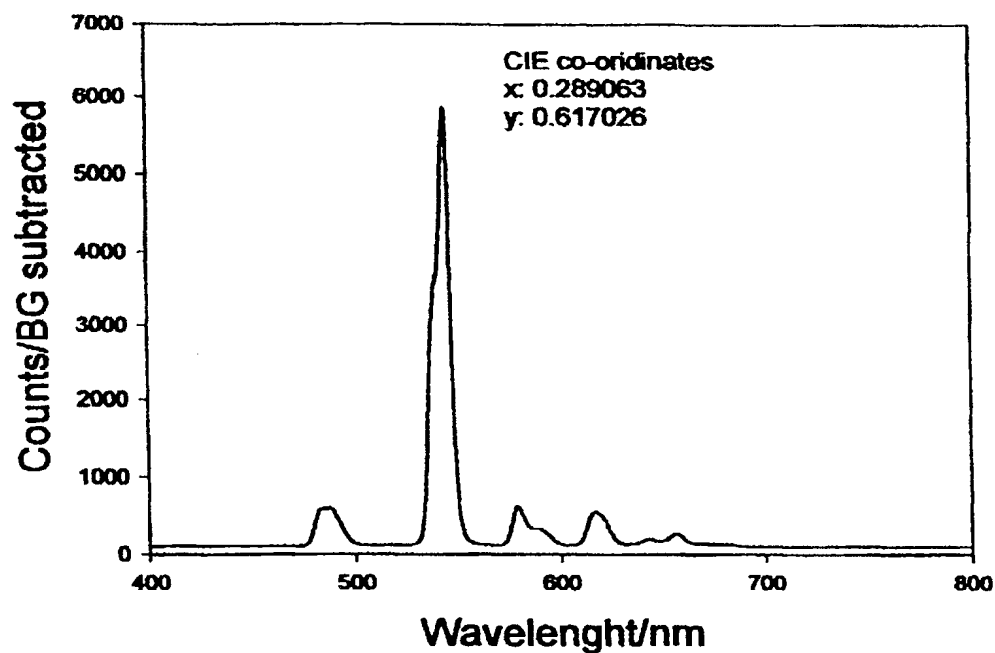


Fig. 1

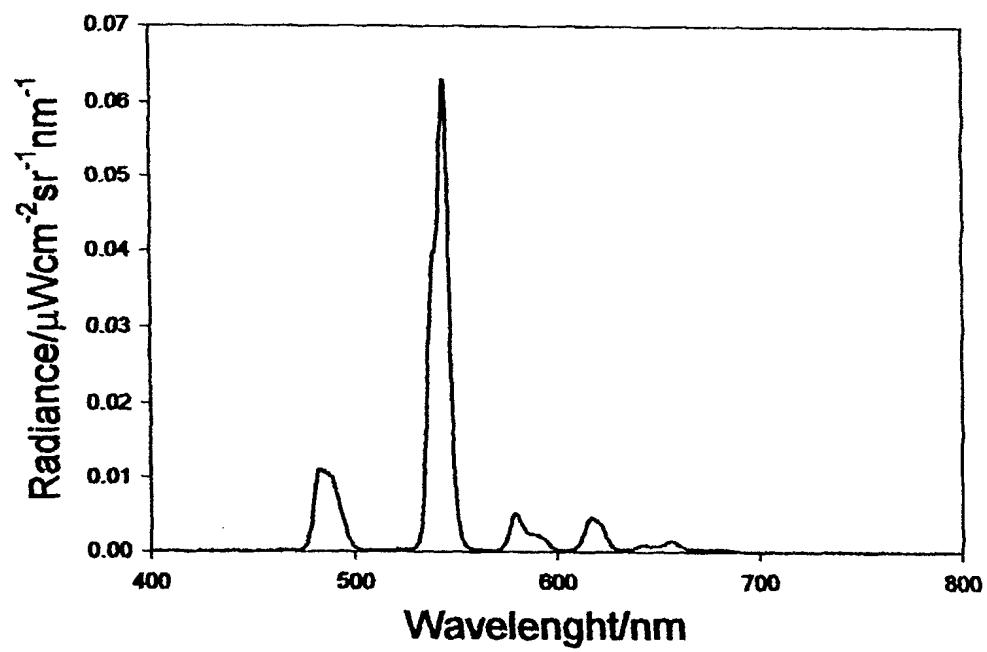
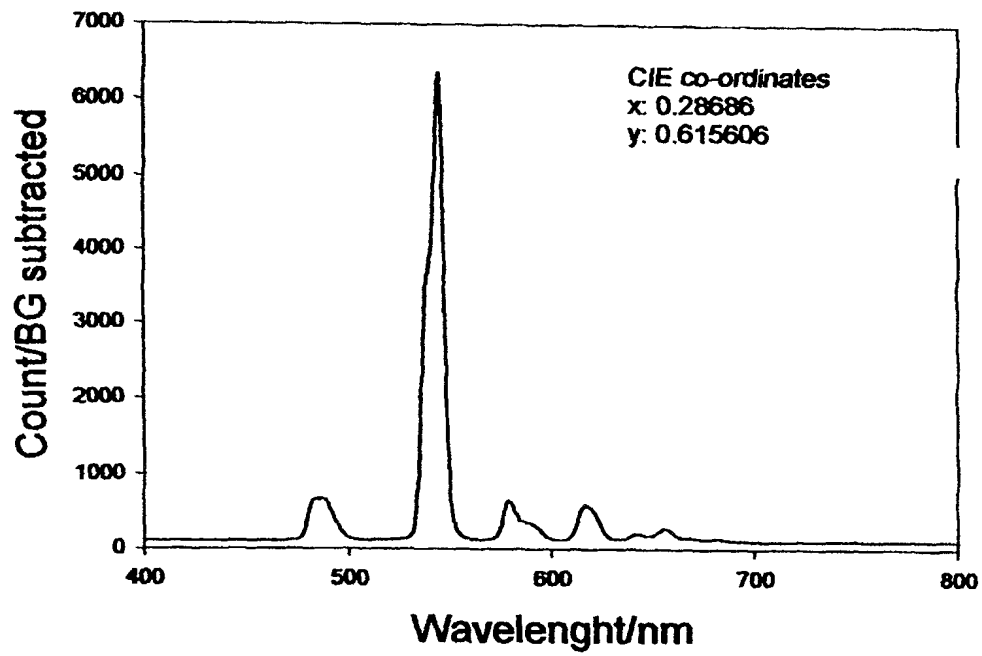


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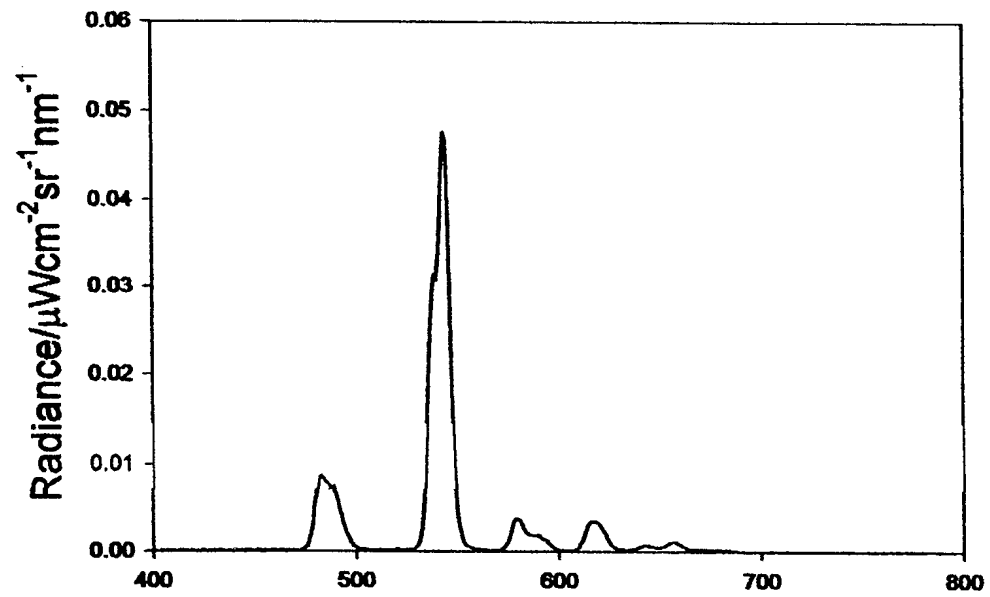
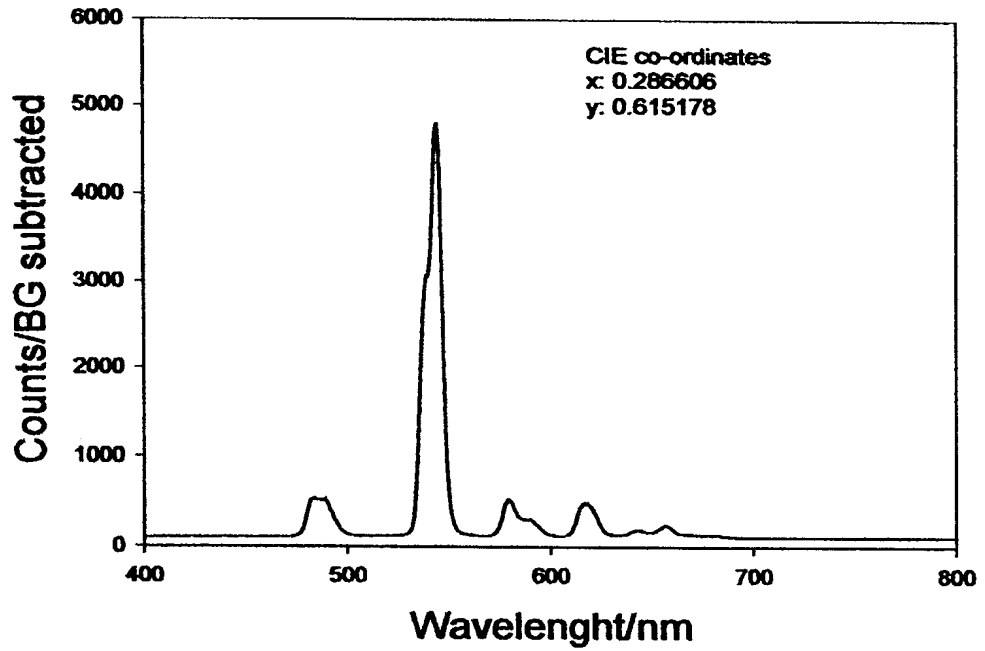
Example 2

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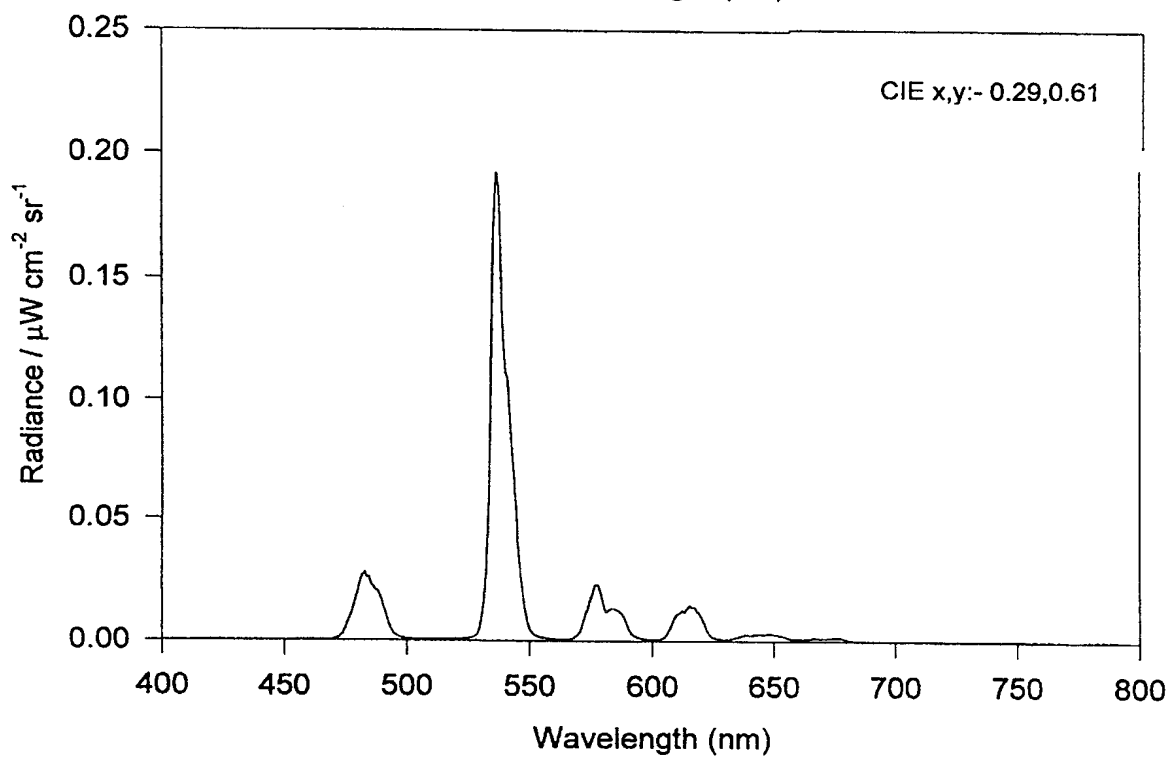
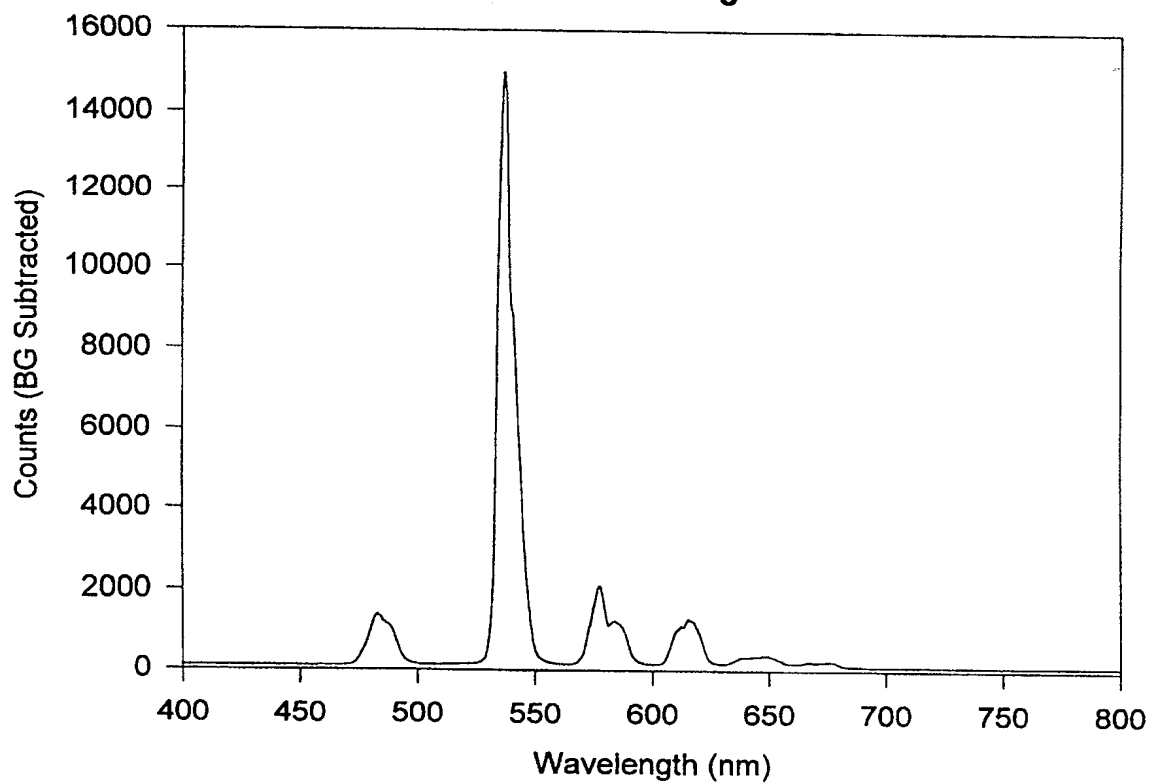
Example 3

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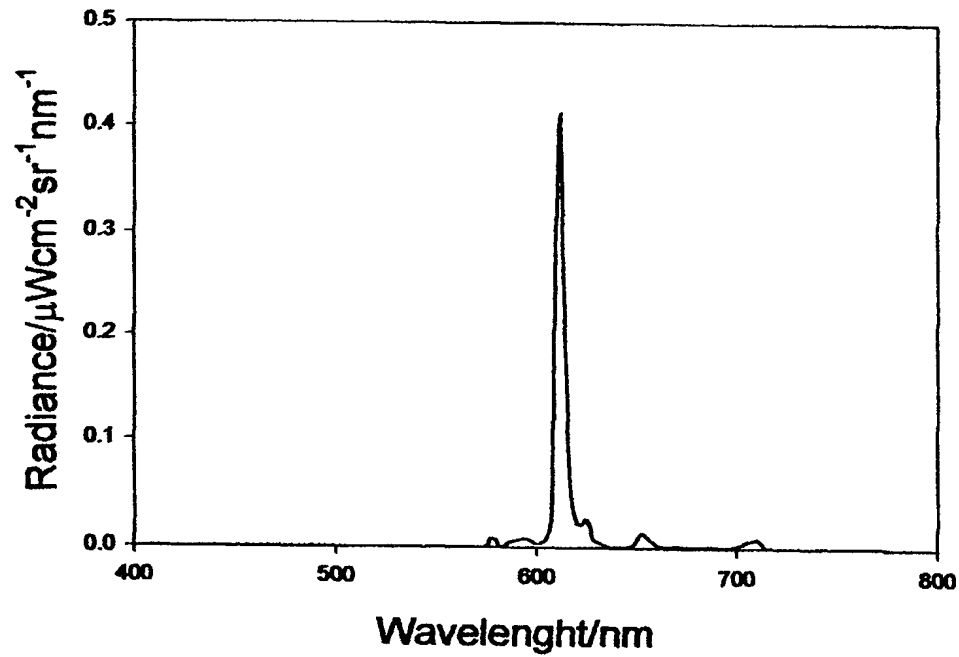
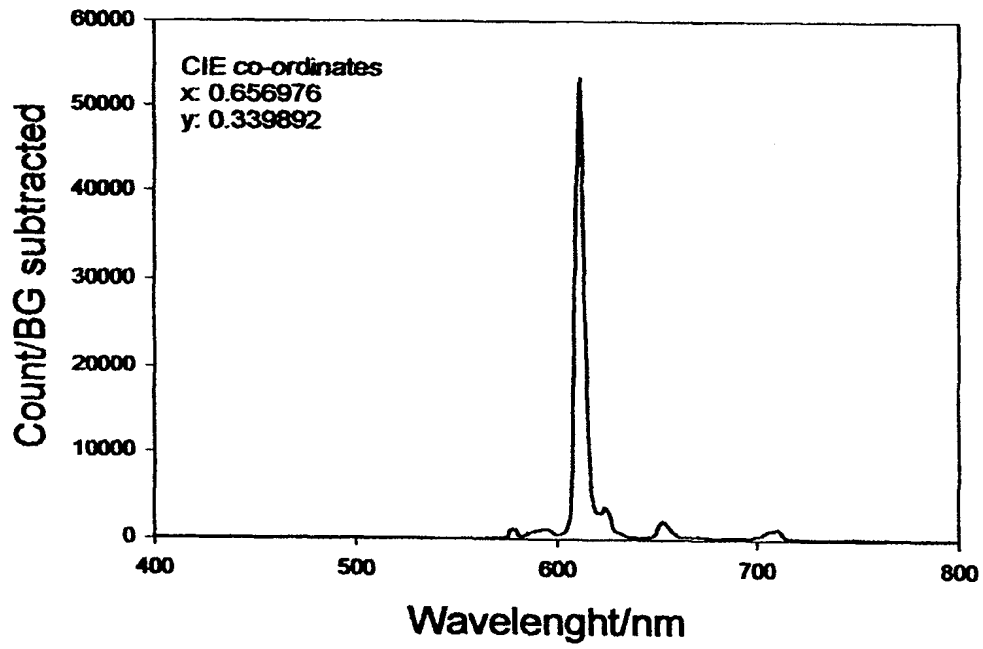
Example 4

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**PL of Tb(TMHD)<sub>3</sub> DPK**

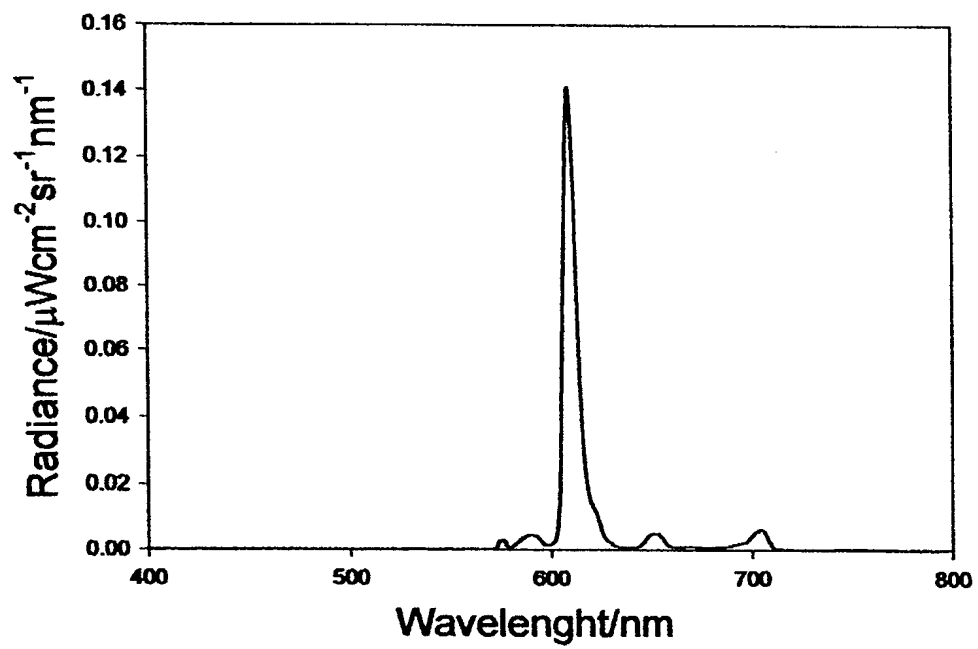
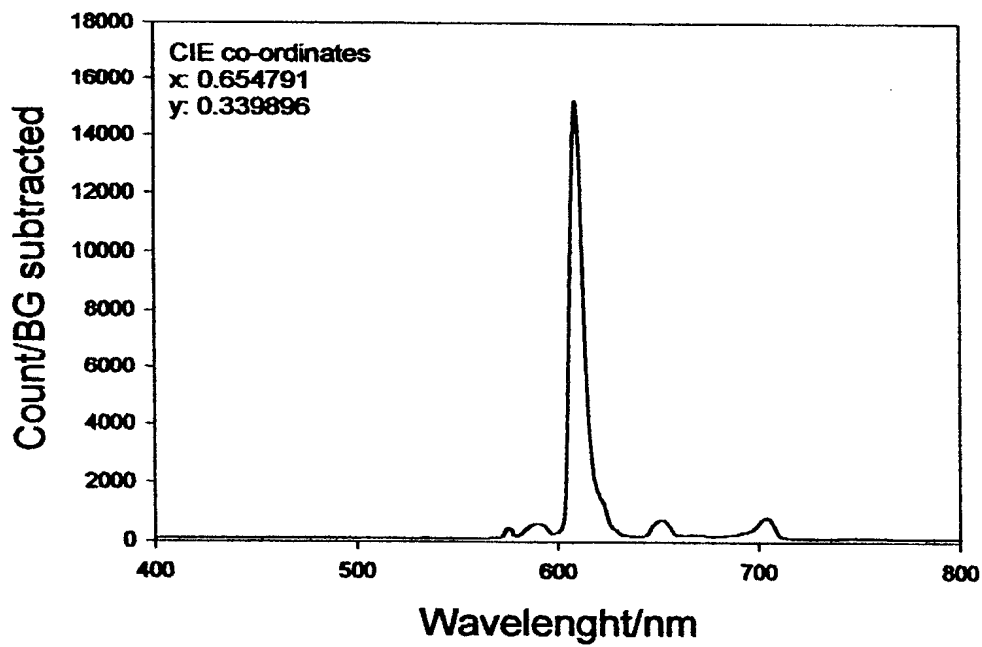
Example 5

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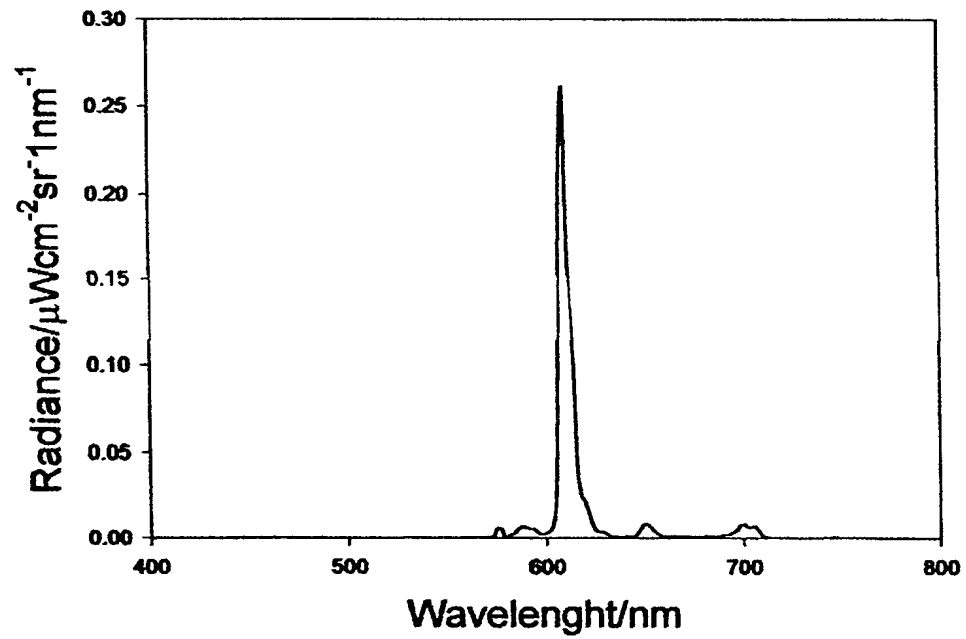
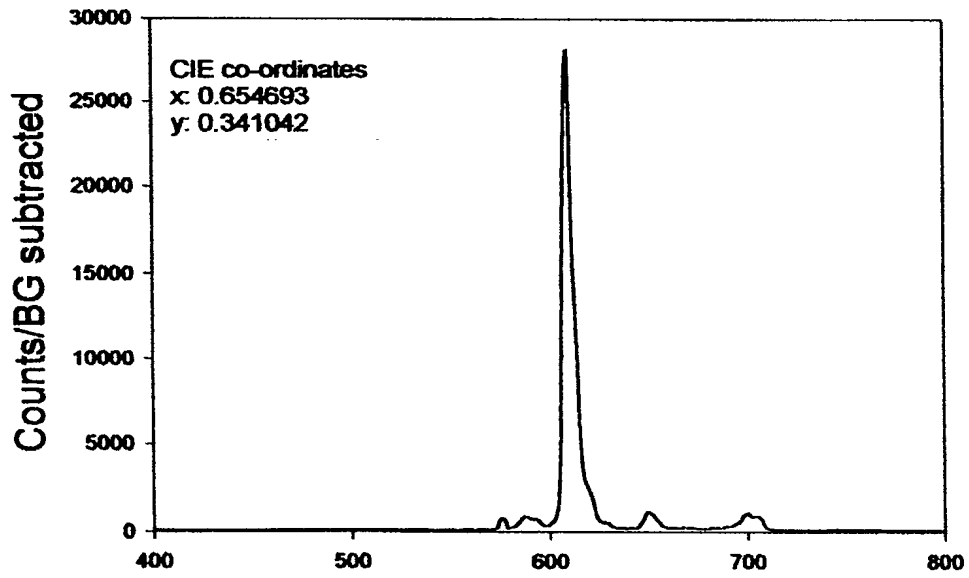
Example 6

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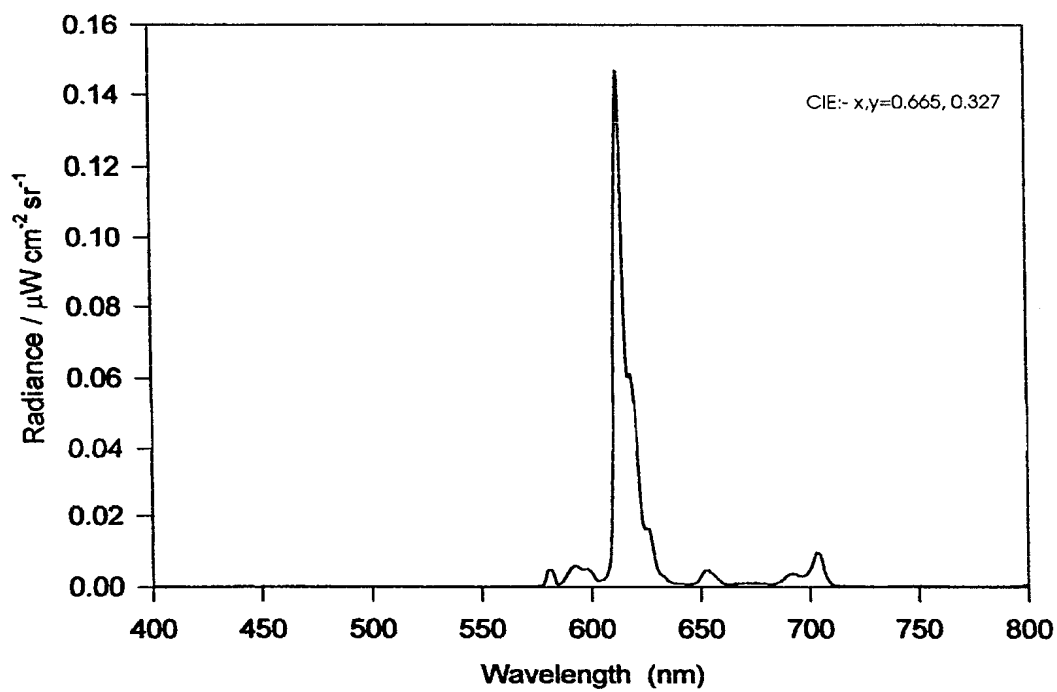
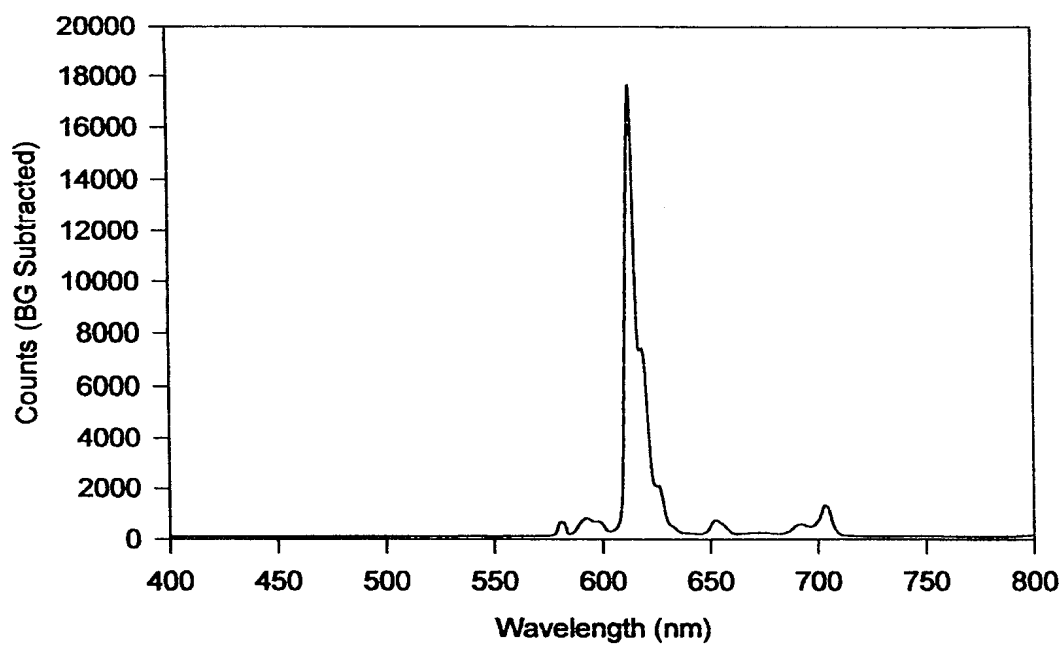
Example 7

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Example 8

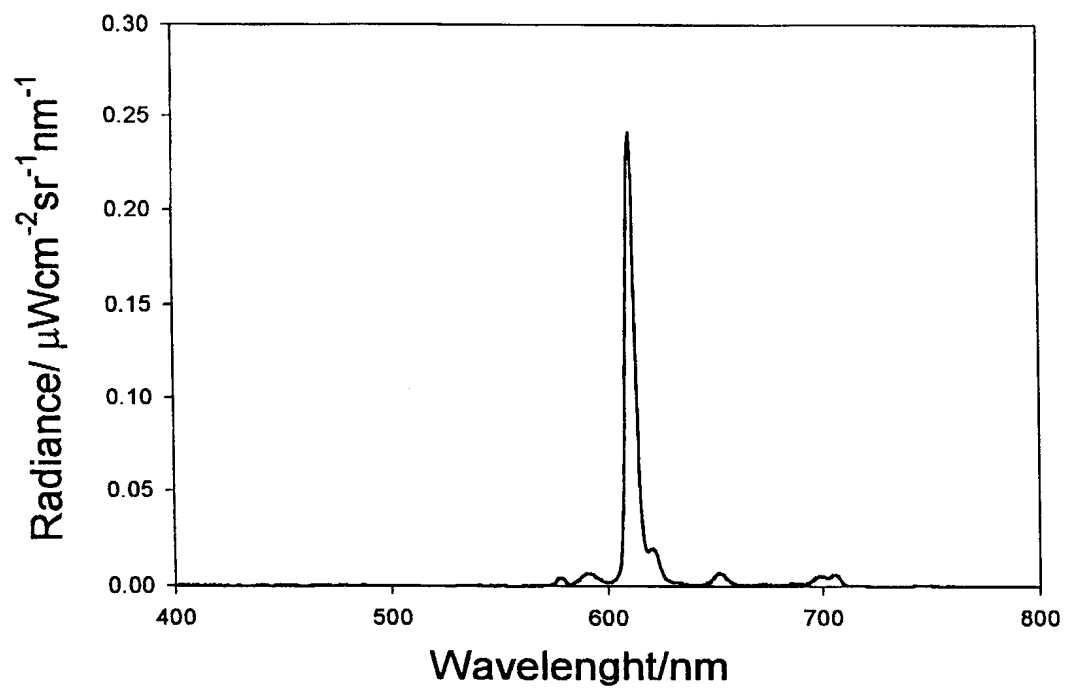
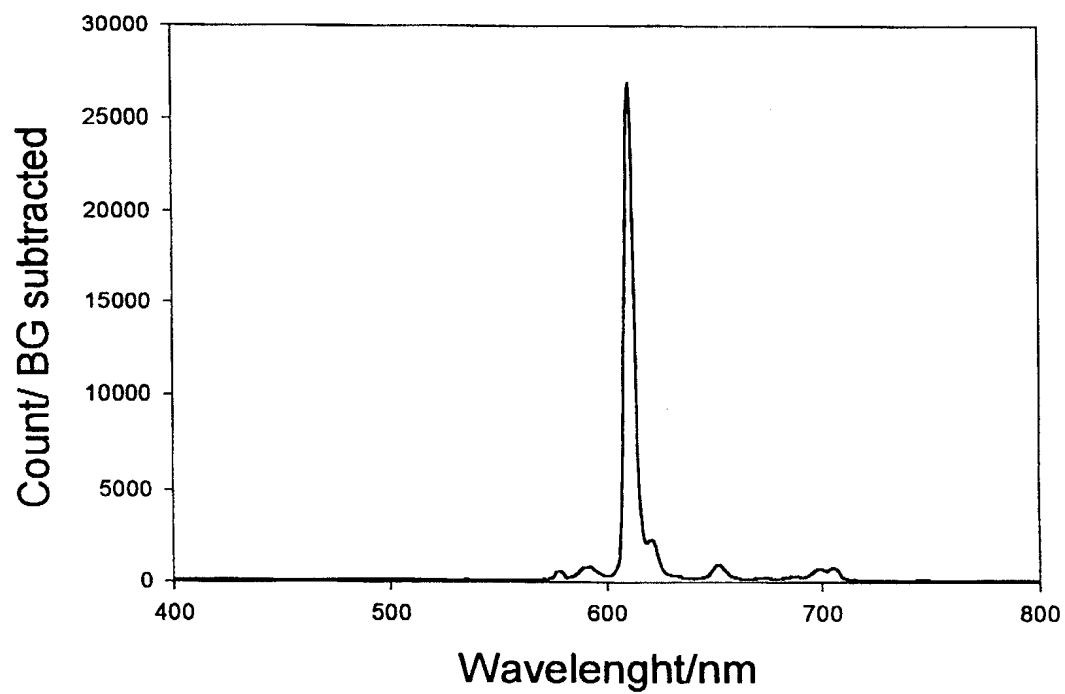
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**PI of Eu(DBM)Bathoplen**

Example 9

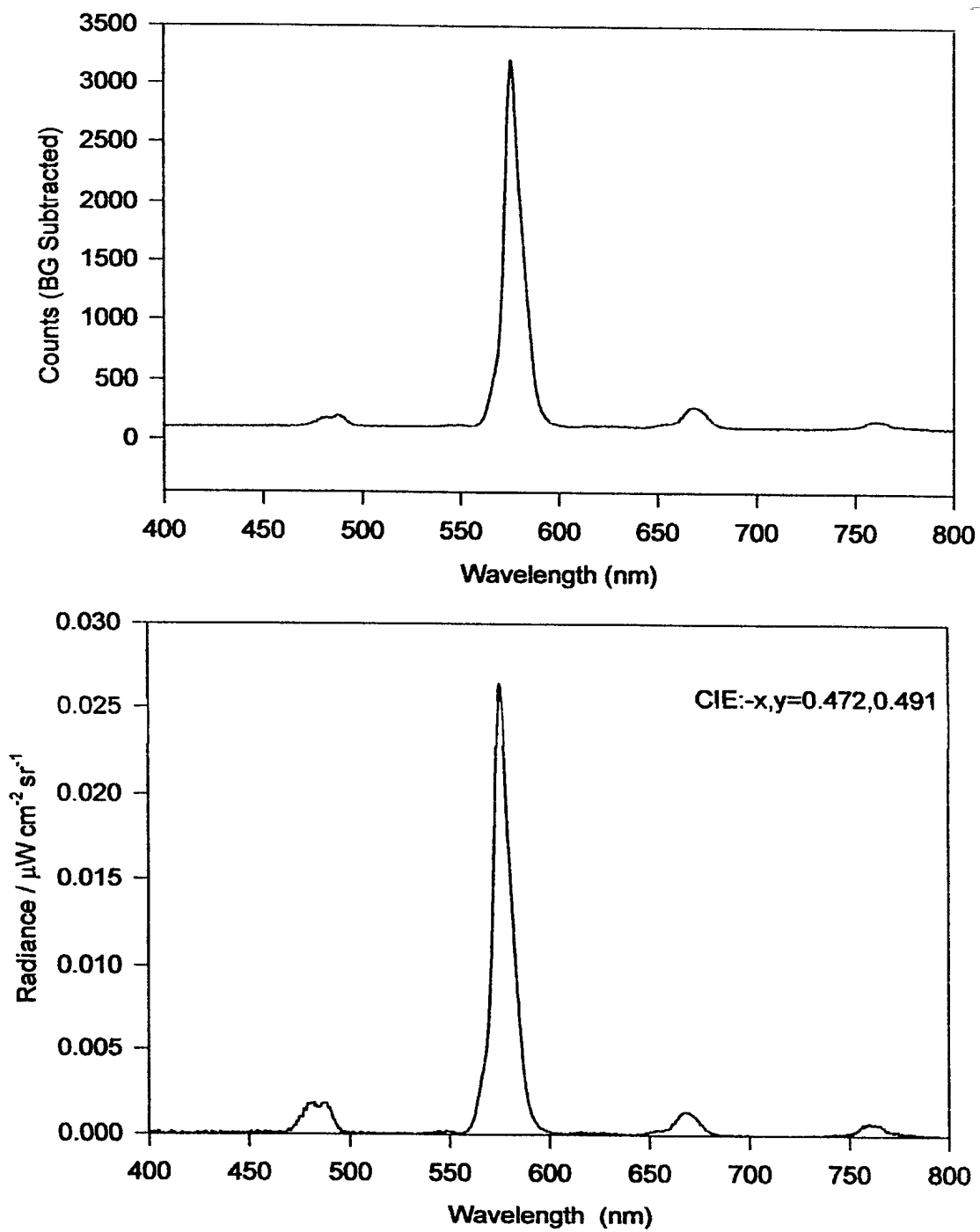


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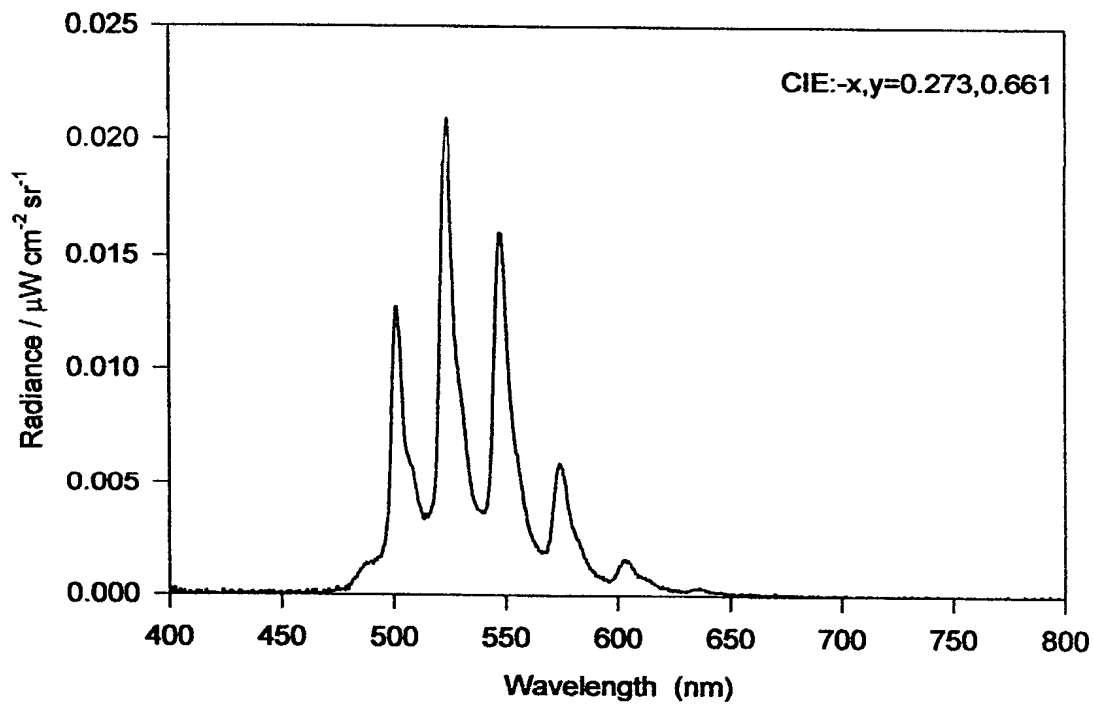
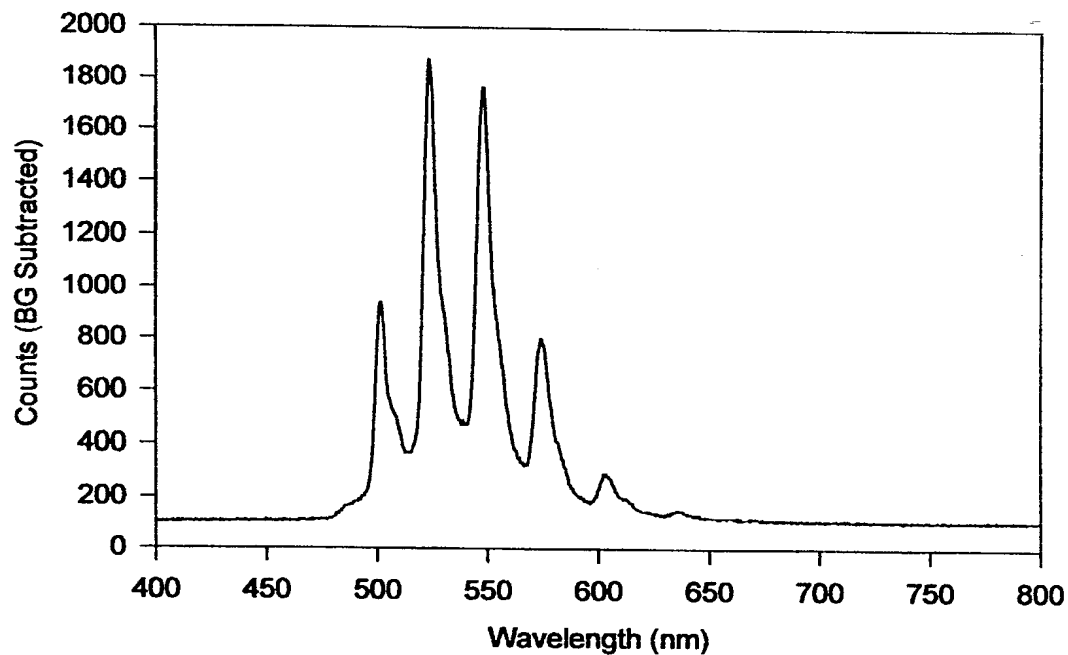
Example 10

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**PI of DyAlp**

Example 11

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**PI of  $\text{UO}_2$** 

Example 12

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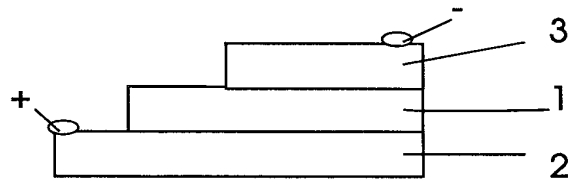


Fig. 13a

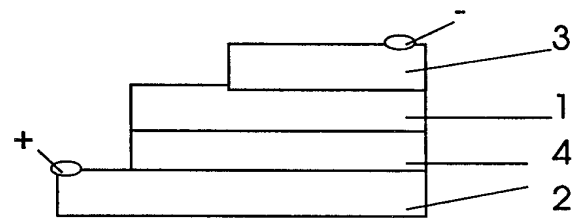


Fig. 13b

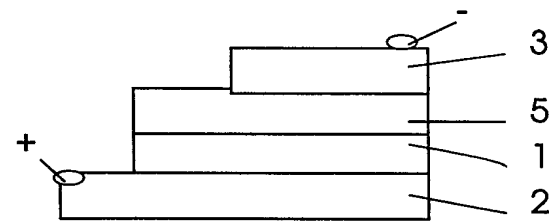


Fig. 13c

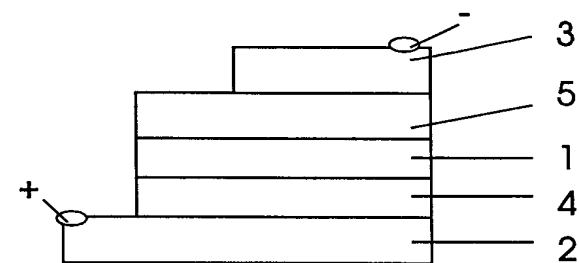


Fig. 13d

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01773

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09K11/06 H05B33/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LIU LIN ET AL: "Europium complexes as emitters in organic electroluminescent devices" INTERNATIONAL CONFERENCE ON ELECTROLUMINESCENCE OF MOLECULAR MATERIALS AND RELATED PHENOMENA, FUKUOKA, JAPAN, 21-24 MAY 1997, vol. 91, no. 1-3, pages 267-269, XP002079652 ISSN 0379-6779, Synthetic Metals, Dec. 1997, Elsevier, Switzerland see figure 1 ---	1-29
X	US 5 128 587 A (KIDO JUNJI ET AL) 7 July 1992 see column 3, line 25 - line 53 --- -/--	1-29



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search

6 October 1998

Date of mailing of the international search report

21/10/1998

Name and mailing address of the ISA

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Fax: (+31-70) 340-3016

Authorized officer

Shade, M

# INTERNATIONAL SEARCH REPORT

Int'l. Application No.

PCT/GB 98/01773

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DIRR S ET AL: "Luminescence enhancement in microcavity organic multilayer structures"</p> <p>INTERNATIONAL CONFERENCE ON ELECTROLUMINESCENCE OF MOLECULAR MATERIALS AND RELATED PHENOMENA, FUKUOKA, JAPAN, 21-24 MAY 1997, vol. 91, no. 1-3, pages 53-56, XP002079653</p> <p>ISSN 0379-6779, Synthetic Metals, Dec. 1997, Elsevier, Switzerland</p> <p>see figures 1,2</p> <p style="text-align: center;">---</p>	26-29
X	<p>KIDO J ET AL: "White-light-emitting organic electroluminescent device using lanthanide complexes"</p> <p>JAPANESE JOURNAL OF APPLIED PHYSICS, PART 2 (LETTERS), 15 MARCH 1996, PUBLICATION OFFICE, JAPANESE JOURNAL APPL. PHYS, JAPAN, vol. 35, no. 3B, pages L394-L396, XP002079654</p> <p>ISSN 0021-4922</p> <p>see figure 1</p> <p style="text-align: center;">---</p>	26-29
X	<p>EP 0 556 005 A (AMERSHAM INT PLC)</p> <p>18 August 1993</p> <p>see the whole document</p> <p style="text-align: center;">---</p>	26-29
A	<p>see the whole document</p> <p style="text-align: center;">---</p>	1-25
X	<p>EP 0 744 451 A (AMERSHAM INT PLC)</p> <p>27 November 1996</p> <p>cited in the application</p> <p style="text-align: center;">---</p>	26-29
A	<p>see the whole document</p> <p style="text-align: center;">---</p>	1-25
A	<p>GREENHAM N C ET AL: "Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers"</p> <p>CHEMICAL PHYSICS LETTERS, 14 JULY 1995, NETHERLANDS, vol. 241, no. 1-2, pages 89-96, XP002079651</p> <p>ISSN 0009-2614</p> <p>cited in the application</p> <p>see page 89 - page 91</p> <p style="text-align: center;">-----</p>	1-29

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Information on patent family members

International Application No

PCT/GB 98/01773

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EP 0744451 A	27-11-1996	NONE	